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Multicomponent Adsorption of Volatile Organic Chemicals onto Granular Activated Carbon

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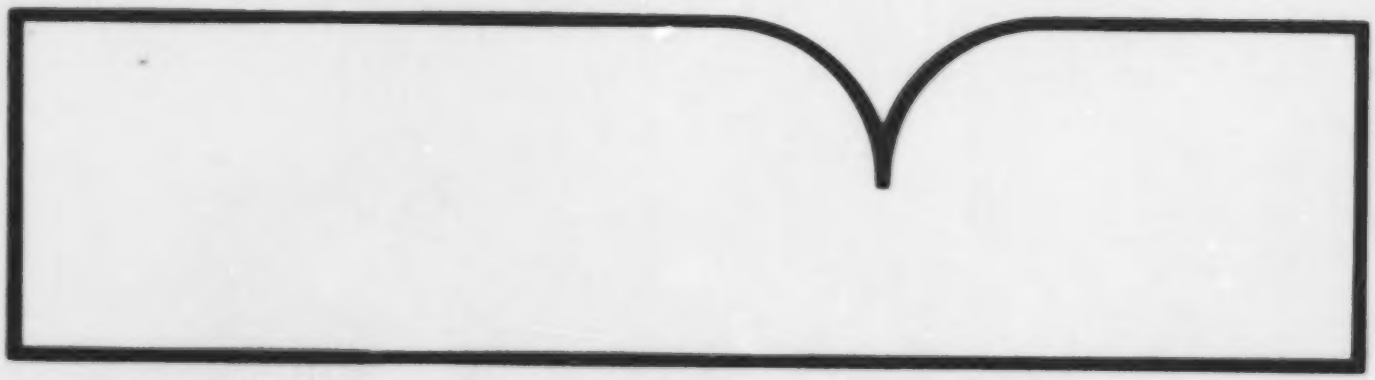

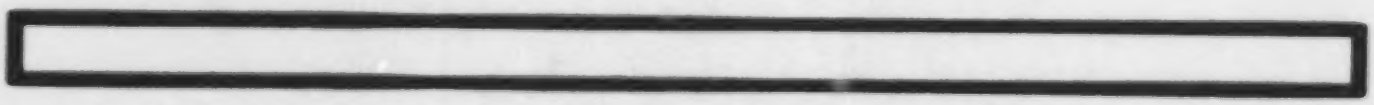

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16. ABSTRACT

A technique has been developed to predict the fixed-bed removal of known SOCs in background mixtures of unknown composition. In addition, this technique was used to relate the removal of important SOCs to nonspecific measures of contamination such as total organic halogen (TOX). In this work, ideal adsorbed solution theory (IAST) was shown to predict the multicomponent isotherm of a six component mixture of volatile organic chemicals (VOCs) which are regarded as toxic groundwater contaminants. In addition, a method of applying IAST to predict known component behavior in a groundwater matrix of unknown composition was verified.

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MULTICOMPONENT ADSORPTION OF VOLATILE ORGANIC CHEMICALS ONTO GRANULAR ACTIVATED CARBON

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INTRODUCTION

Granular activated carbon (GAC) is a promising technique for removal of some synthetic organic chemicals (SOCs); however, it can be a relatively expensive process. In order to reduce costs, techniques need to be developed to predict process performance so that the cheapest process operation may be selected. With few exceptions, most of the predictive mathematical modeling work has focused on mixtures of known composition. Unfortunately, drinking water and wastewater contains many competing organic solutes and most of them will never be identified. Accordingly, a technique has been developed to predict the fixed-bed removal of known SOCs in background mixtures of unknown composition. In addition, this technique was used to relate the removal of important SOCs to nonspecific measures of contamination such as total organic halogen (TOX). (Crittenden et al., 1984)

In this work, ideal adsorbed solution theory (IAST) was shown to predict the multicomponent isotherm of a six component mixture of volatile organic chemicals (VOCs) which are regarded as toxic groundwater contaminants. In addition, a method of applying IAST to predict known component behavior in a groundwater matrix of unknown composition was verified. The competitive adsorption effects of the unknown background are accounted for by two pseudo-components. The pseudo-components are theoretical components that are used in the IAST calculations to account for the competitive effects of the unknown background.

EXPERIMENTAL PROCEDURE

Bottle Point Isotherm. Bottle point isotherm experiments were conducted by adding varying amounts of powdered GAC (200X400 mesh) to serum bottles. The bottles were then filled head-space free with water containing the VOCs. The bottles were capped and equilibrated at constant temperature by rotating them at 25 rpms for at least 6 days. These solutions were buffered with .001 M phosphate buffer at a pH of 6.0. After equilibration, the serum bottles were centrifuged to remove the PGAC and the equilibrium liquid-phase concentration, C_l, was determined by liquid-liquid extraction and gas chromatography. The adsorbent-phase concentration, q_l, was determined from this mass balance:

$$q_l = V[C_{lo} - C_l]/M \qquad (1)$$

In which V is the bottle volume, and M is the dosage of PGAC.

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Single Solute Isotherm Data Analysis. The single solute isotherm data was fit to the Freundlich adsorption isotherm equation:

$$q_i = K_i C_i^{1/n_i} \qquad (2)$$

In which, K_i and $1/n_i$ are the Freundlich isotherm parameters for adsorbate i.

The data was transformed by taking the logarithm of C_i and q_i and fitting these transformed data by the least squares method. The slope of this line is $1/n_i$ and the intercept is K_i.

Single Solute Results. The single solute isotherm parameters and their 95% confidence limits for the the VOCs are given in Table 1. A typical single solute isotherm plot (ethylene dibromide) is shown in Figure 1. 95% confidence limits are not shown because they are small.

PREDICTION OF MULTICOMPONENT EQUILIBRIA OF KNOWN MIXTURES

Mathematical Approach. When all the compounds present in the water have been identified and quantified, it is possible to use IAST to predict the multicomponent equilibrium conditions from single solute adsorption isotherms of the adsorbates (Radke and Prausnitz, 1972; Jossens et al., 1978; Fritz et al., 1981).

The IAST development is analagous to Raoult's law for vapor-liquid equilibria. For IAST, the concentration in solution C_i is related to the mole fraction on the surface of the carbon, z_i, and the single solute concentration, C_i^o, that gives the identical surface tension at the adsorbent surface as in the multicomponent mixture.

$$C_i = z_i C_i^o \qquad (3)$$

If the Freundlich isotherm equation is used to represent single solute behavior, the IAST yields the following equation for each adsorbate.

$$C_i = z_i \left[\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right]^{n_i} \qquad (4)$$

In which, N is the number of components and n_i is the reciprocal of the Freundlich isotherm parameter, $1/n_i$. Equation 4 does not account for the Henry's Law region in the estimation of spreading pressure, but usually this has a negligible effect which was demonstrated using the modification which was proposed by Singer and Chen-Yu (1980).

By combining Equation 4 with the mass balance, Equation 1, the liquid-phase concentration, C_i, was eliminated. For each component in the mixture an equation of that form was written, yielding N equations and N unknowns for the adsorbent-phase concentrations, q_i. These equations were solved using a Newton-Raphson algorithm. By specifying the initial concentrations, carbon dosages, bottle volume

and single solute isotherm parameters, the multicomponent isotherm concentrations were calculated.

Known Mixture Results. A known mixture was made up by spiking organic free water with these six components with initial concentrations ranging from 12 to 14 uM/L: (a) tetrachloroethene, (b) trichloroethene, (c) bromoform, (d) 1,2-dibromoethane, (e) chlorodibromomethane, and (f) chloroform. This solution was added to bottles containing varing amounts of PGAC as described in the bottle point procedure.

Figures 2-4 compare the single solute isotherms, multicomponent component data and IAST predictions for only three of the six components which were initially present in the mixture. The equilibrium conditions for each carbon dosage which was calculated using IAST are marked on Figures 2-4 and they may be compared to the data which are plotted. The trends in equilibrium concentrations which were predicted by IAST may be seen from the curves which connect the IAST predictions for other PGAC dosages. These results demonstrate that IAST gives good agreement with the data.

PREDICTION OF MULTICOMPONENT EQUILIBRIA OF UNKNOWN MIXTURES

From a practical point of view, it would be impossible to identify and quantify all the background components that cause competitive interaction with the VOCs that are to be removed. For this reason the "pseudo-component" approach has been developed. This approach is similar to that proposed by Frick and Sontheimer (1983) and Hubele and Sontheimer (1983). However in this study, the simplified competitive adsorption model was not used and methods for determining the mass transfer coefficients of the pseudo-compounds were proposed elsewhere (Crittenden *et al.*,1984).

Mathematical Approach. Ideal adsorbed solution theory, Equation 4, has been shown to predict multicomponent competition. In the pseudo-component model, the displacement of a known tracer component in the presence of the background from its single solute isotherm was used to calculate the competitive effect of the unknown components in the background.

To determine the pseudo-component properties, an isotherm was conducted for a known component (usually a component which is to be removed) in the presence of the unknown background. By using this equilibrium data and the single solute Freundlich parameters of this known component (K_1, $1/n_1$), a parameter search algorithm is employed to find pseudo-component parameters that describe the competition of unknown components in the background. IAST is used to describe the competitive adsorption effects of the psuedo-components with the known component. The necessary pseudo-component parameters which must be determined are their Freundlich parameters, K_2, K_3, $1/n_1$, and $1/n_2$, and initial concentrations, C_{2o} and C_{3o}.

Once the pseudo-component parameters are determined using a tracer component, the identical parameters were used to predict competitive interactions with the background for other known

components. Accordingly, the competition due to unknown components in the background were predicted for any known component from single solute isotherm parameters for that component and pseudo-component properties which were determined for one tracer component.

Experimental Results. The pseudo-component approach was applied to a contaminated groundwater which was obtained from a city in the midwest. The major contaminants of interest (in high concentration) included cis-dichloroethene (DCE), trichloroethene (TCE), and tetrachloroethene (PCE). Single solute isotherms were conducted in organic free water and the results are reported in Table 1. Isotherms were also conducted for the three components in the presence of the groundwater matrix. Two pseudo-components were used to describe the competitive interactions between the unknown components in the groundwater matrix and DCE. These results are shown in Figure 5. To verify that the pseudo components adequately represent the competitive background, these identical pseudo-components were used to predict the competitive interactions between TCE (Figure 6) and the unknown background. In addition to the work which is shown in Figures 5-6, this procedure was repeated for another carbon. In both cases, the predicted competitive interactions with the unknown components in the groundwater agreed reasonably well with the data.

These results suggest that competitive interactions between known components and unknown components in the background water matrix may be predicted by conducting one isotherm experiment in the unknown background for a known component (in this case, DCE).

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Table 1. Single Solute Parameters.

Carbon Type, Size, Temperature, Water Matrix	Compound	Equilibration time, pH	K(ug/g)(L/ug)$^{1/n}$ Best Fit	95% Confidence Interval K	1/n Best Fit	95% Confidence Interval	Concentration Range ug/L
F-400	Cis-Dichloroethene	7 days pH=6.0	150.7	121.4-187.2	0.7045	0.6687-0.7402	120-1250
400<R<200 Mesh	Trichloroethene	6.5 days pH=6.0	3389.7	2795.6-4109.9	0.4163	0.3620-0.4706	5.6-360
9-11°C	Tetrachloroethene	6 days pH=6.0	10388.8	9443.1-11429.2	0.4579	0.4365-0.4794	3.5-1170
	Bromoform	10 days pH=6.0	1802.0	1696.2-1914.4	0.5629	0.5528-0.5730	40.0-2000
	Chloroform	7 days pH=6.0	284.8	254.7-318.4	0.5325	0.5102-0.5549	8.0-1180
	1-2,DiBromoethane	7 days pH=6.0	1795.0	1632.6-1973.5	0.4808	0.4637-0.4979	32.0-1750
	Chlorodibromomethane	7 days pH=6.0	1265.7	981.7-1631.8	0.5170	0.4758-0.5581	92.0-1830

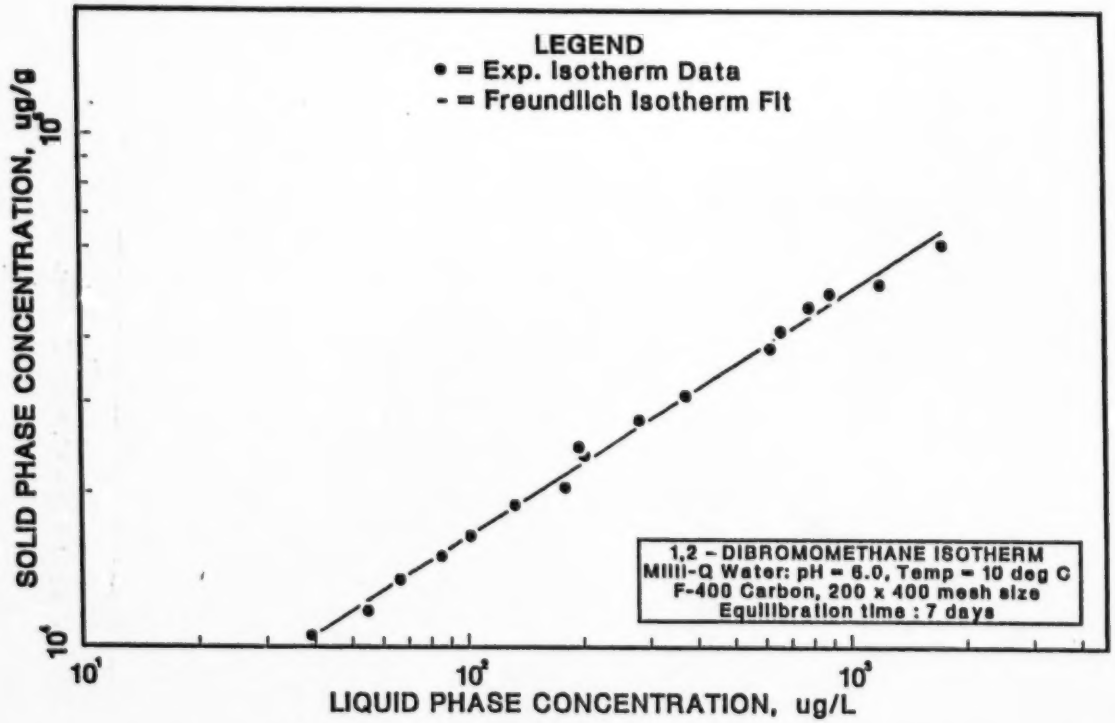

Figure 1. Single solute adsorption isotherm data for 1,2-dibromoethane and the best fit Freundlich isotherm equation.

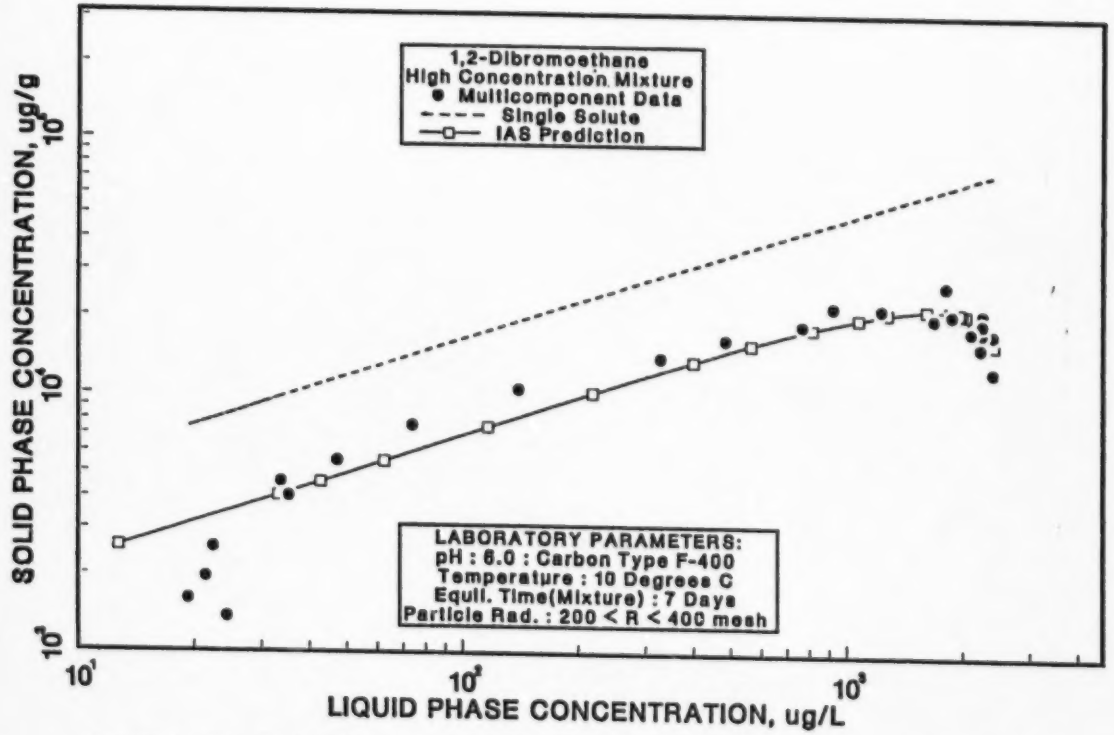

Figure 2. The single solute isotherm equation, multicomponent isotherm data for chloroform in the presence of tetrachloroethene, trichloroethene, bromoform, 1,2-dibromoethane, and chlorodibromomethane. and ideal adsorbed solution theory predicted results.

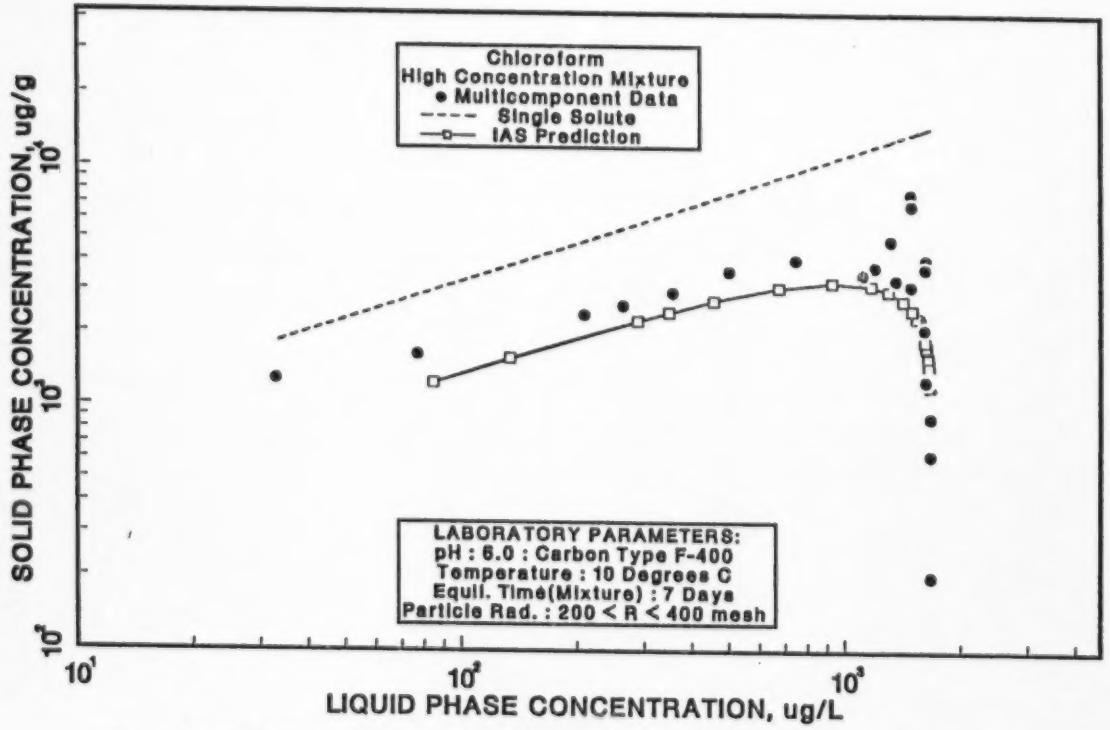

Figure 3. The single solute isotherm equation, multicomponent isotherm data for 1,2-dibromoethane in the presence of tetrachloroethene, trichloroethene, bromoform, chloroform and chlorodibromomethane, and ideal adsorbed solution theory predicted results.

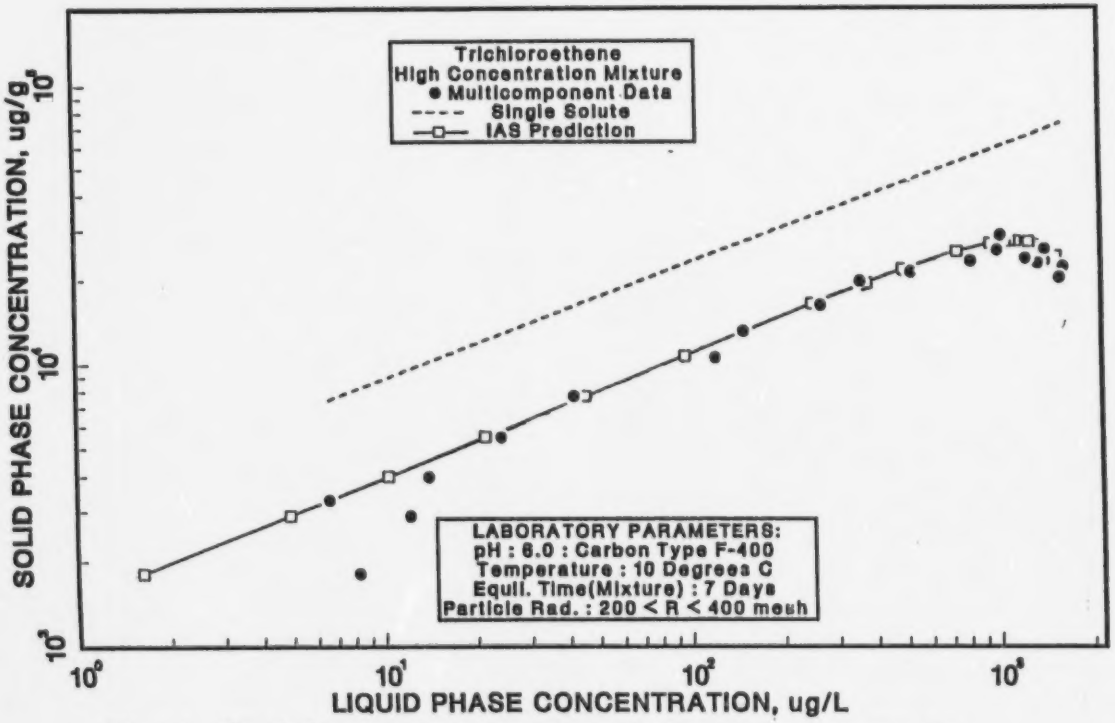

Figure 4. The single solute isotherm equation, multicomponent isotherm data for trichloroethene in the presence of tetrachloroethene, 1,2-dibromoethane bromoform, chloroform and chlorodibromomethane, and ideal adsorbed solution theory predicted results.

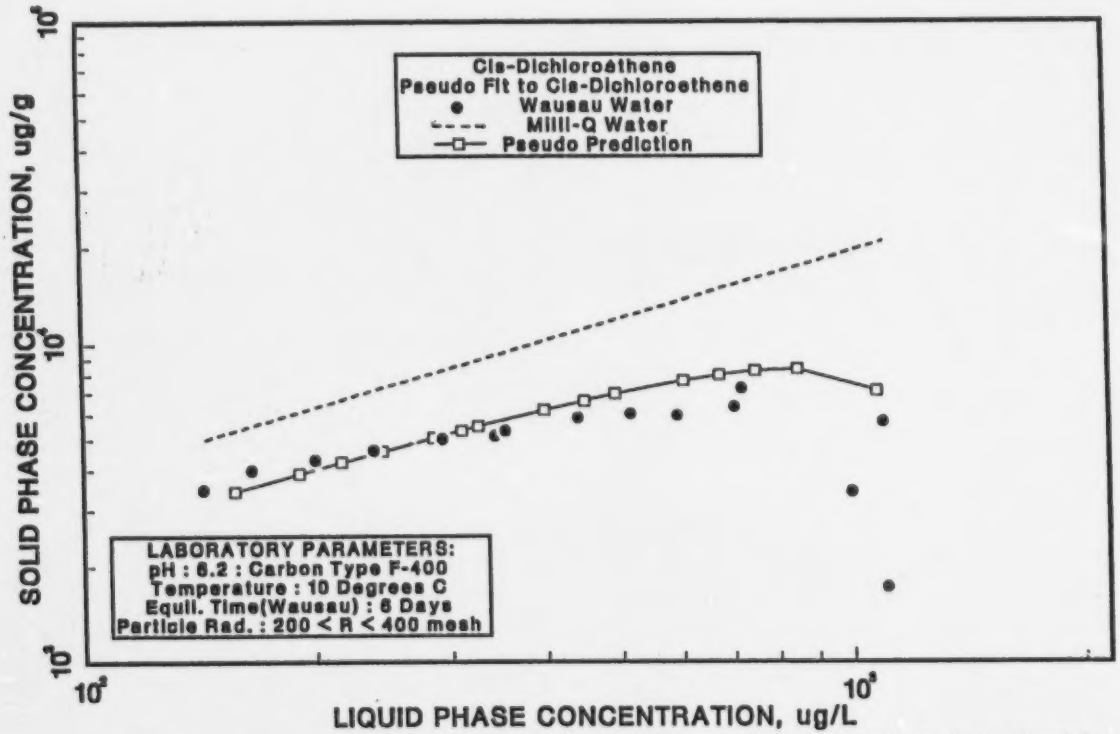

Figure 5. Isotherm data for cis-dichloroethene which was collected in the background matrix of the contaminated groundwater and a fit of these data using two psuedo-components to represent the competitive interactions of the background.

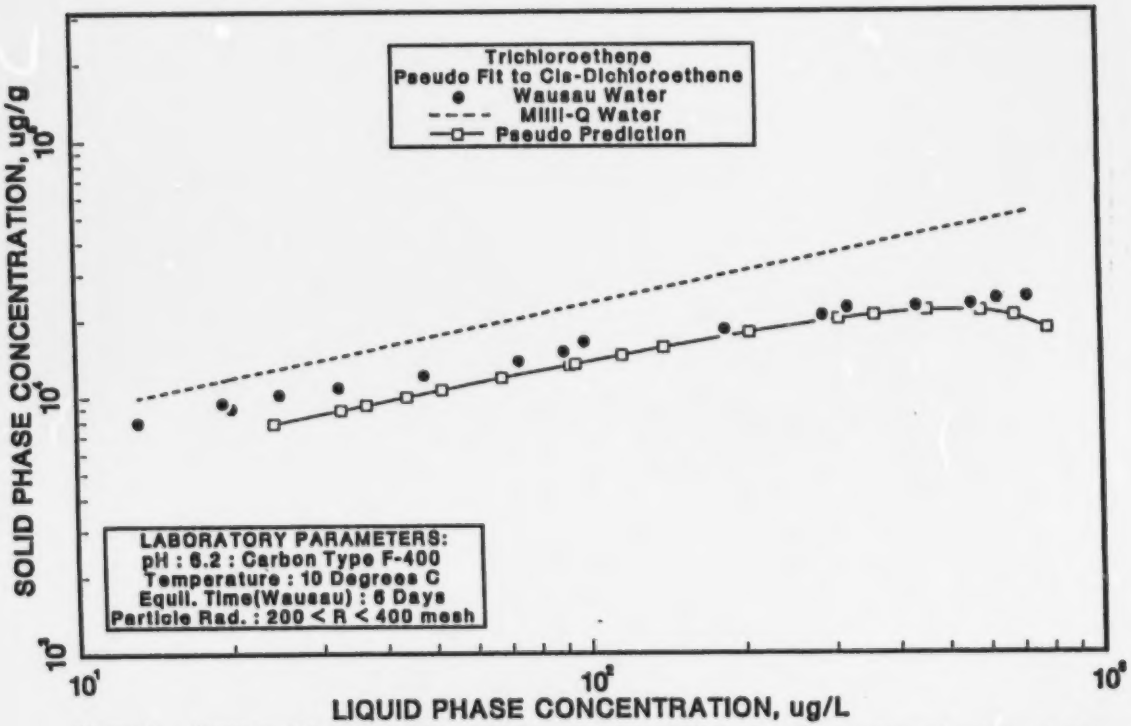

Figure 6. Isotherm data for trichloroethene which was collected in the background matrix of the contaminated groundwater and a prediction of the background competition using the two psuedo-components that were determined from the cis-dichloroethene isotherm data (Figure 5).